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Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

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REST-BREAKING COMPOSITION AND USE THEREOF

The invention relates to a rest-breaking composition and the use thereof.

- 5 Deciduous fruit species require winter chilling to grow normally. The amount of chilling required depends upon the kind of fruit and the cultivar. If winter chilling is insufficient, then growth abnormalities such as delayed and uneven blossoming, poor leaf cover, insufficient fruit set, and reduced fruit size can occur. These symptoms are generally referred to as delayed foliation according
- 10 to the article by K.L.J. Blommaert, "Winter Dormancy and Delayed Foliation," *The Deciduous Fruit Grower* (1956).

- Measures to reduce the symptoms of delayed foliation include treatment with rest-breaking agents during later winter and various physical manipulations
- 15 such as pruning. In South Africa, for example, most apple trees receive insufficient winter chilling to break rest completely and thus annual application of a rest-breaking agent is standard practice.

- The rest-breaking agents that are used nowadays in commercial orchards are
- 20 either organic nitrogen-containing compounds or inorganic nitrates.

- The most widely used organic nitrogen-containing rest-breaking agents are dinitro-ortho-cresol (DNOC) in combination with oil and hydrogen cyanamide in combination with oil (e.g. Dormex®). The oil in these compositions is used to allow an even distribution of the agent over the species to be treated. It is to be
- 25 noted that although DNOC/oil and hydrogen cyanamide/oil compositions are effective at breaking rest in deciduous fruit species, DNOC is harmful to the environment and its use is prohibited in Europe and the United States, and hydrogen cyanamide is toxic to man, limiting its use in certain rest-breaking applications.

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One of the known inorganic nitrate rest-breaking agents is potassium nitrate, which has been shown to have a positive effect on peaches. However, potassium nitrate is not as effective as DNOC or hydrogen cyanamide. It is to be noted that deciduous fruit species with a high chill requirement, such as grapes, require a relatively high concentration of such a rest-breaking agent.

WO 94/23574 describes additives which promote the activity of rest-breaking agents such as hydrogen cyanamide and potassium nitrate. These additives are alkoxylated amines (e.g. Armoblen®) and alkoxylated quaternary ammonium compounds.

WO 96/01049 and WO 97/24926 describe the use of the aforementioned types of additives (additionally disclosing the use of Armobreak®) in combination with hydrogen cyanamide and several inorganic salt rest-breaking agents, i.e., potassium nitrate, ammonium nitrate, calcium nitrate, urea ammonium nitrate, calcium ammonium nitrate, and zinc ammonium nitrate, and mixtures thereof.

Although the compositions described in the aforementioned international patent publications effectively break the rest in various deciduous fruit species, they do not reach the desired level of uniformity of bud break nor the desired balance of vegetative and reproductive bud break.

GB-A-2 059 412 describes the application of an aqueous solution of a choline salt to enhance the reproductive development of plants including deciduous fruit trees such as apple, pear, plum, and peach trees. It is described that treatment of deciduous fruit trees results in break of dormancy.

However, as is shown in the Examples of the present patent application, the use of only a choline salt in combination with a surfactant does not give the desired rest-breaking activity either.

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For the foregoing reasons, there is still a need in the art for improved rest-breaking compositions which are effective, less toxic than the most-effective compositions that are known in the art of rest-breaking, which can be employed
5 at economically and environmentally acceptable concentrations of the active ingredients, and which are non-hazardous to operators.

The present invention relates to a composition useful for the breaking of rest in deciduous fruit species comprising an organic nitrogen-containing compound
10 having a molecular weight of 60 to 300 with the exception of urea and dinitro-ortho-cresol, an inorganic nitrate, and a surfactant.

The use of the composition of the present invention for breaking the rest of deciduous fruit species produces improvements in advancing the time of bloom,
15 bud break and/or leaf cover and fruit set.

In Table 1 of the present application, the percentage of overall bud break is presented as a representative parameter for evaluating the rest-breaking activity of a given composition.

20 In the context of the present invention, by the term "deciduous fruit species" is meant any species which requires the use of a rest-breaking agent due to delayed foliation, in order to improve the yield and quality of the fruit in regions which have mild winter weather conditions.

Besides the term rest-breaking agent, the terms dormancy-breaking agent and
25 bud-breaking agent are also used frequently in this field of technology.

Typical examples of deciduous fruit species include apples, pears, peaches, apricots, plums, cherries, grapes, vines, kiwis, nectarines, and almonds.

Preferably, the organic nitrogen-containing compound has a molecular weight
30 of 60 to 250, more preferably 60 to 200, and most preferably 60 to 150.

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Typical examples of the organic nitrogen-containing compound rest-breaking agent in accordance with the present invention include ethylenediamine, (C₁-C₃)alkylated ethylenediamines such as N-methyl-ethylenediamine and N,N-diethylethylenediamine, ethanolamine, (C₁-C₃)alkylated ethanolamines such as N-methylethanolamine and N,N-diethylethanolamine, (carboxymethyl)tri-(C₁-C₃)alkylammonium salts such as (carboxymethyl)trimethylammonium hydroxide inner salt or betaine and 1-carboxy-N,N,N-trimethanaminium chloride or betaine hydrochloride, (2-hydroxyethyl)tri(C₁-C₃)alkylammonium salts such as (2-hydroxyethyl)trimethylammonium or choline chloride, (2-hydroxy-propyl)tri(C₁-C₃)alkylammonium salts, (2-hydroxybutyl)tri(C₁-C₃)alkyl-ammonium salts, and mixtures thereof.

The C₁-C₃-alkyl group preferably is a methyl or ethyl group, most preferably a methyl group. The term salt in the aforementioned classes of compounds is well known to the person skilled in the art and it typically refers to a halide ion such as a chloride ion or a (methyl)sulfate ion.

Preferably, the organic nitrogen-containing compound is selected from the group consisting of ethylenediamine, N-methyl-ethylenediamine, N,N-diethylethylenediamine, ethanolamine, N-methylethanolamine, N,N-diethylethanolamine, betaine, betaine hydrochloride, and choline salts. Most preferably, it is a choline salt.

Typical examples of choline salts which can be used in the composition of the invention include choline chloride, choline nitrate, choline phosphate, choline sulfate, choline bitartrate, choline dihydrogen citrate, tricholine citrate, choline bicarbonate, choline carbonate, and mixtures thereof. The use of choline chloride is particularly preferred.

It is to be understood that not all compounds may work on all deciduous fruit species in all orchards. For example, it was found that choline borate could not

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be used on Golden Delicious apples in South Africa. By routine experimentation one of ordinary skill in the art can establish, however, which compounds produce the desired rest-breaking effect and which do not.

- 5 Typical examples of inorganic nitrate salts or nitrogen fertilizers which can be used in the composition of the invention include alkali metal and earth alkali metal nitrates such as sodium nitrate, potassium nitrate, and calcium nitrate, ammonium nitrates such as ammonium nitrate itself, calcium ammonium nitrate, urea ammonium nitrate, and zinc ammonium nitrate, and mixtures thereof. The
- 10 latter three sources of ammonium nitrate essentially eliminate the explosion hazard of ammonium nitrate and have better storage and handling properties and are known in the art (Kirk-Othmer *Encyclopedia of Chemical Technology*, Third Edition, Vol. 10, John Wiley & Sons, New York, 1980, pages 47-56). Preferably, the inorganic nitrate rest-breaking agent is selected from the group
- 15 consisting of potassium nitrate, calcium nitrate, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, zinc ammonium nitrate, and mixtures thereof. The use of calcium nitrate, calcium ammonium nitrate, urea ammonium nitrate, and mixtures thereof is particularly preferred.

- 20 In the context of the present invention, by the term "surfactant" is meant any compound which improves the distribution of the rest-breaking agents over the deciduous fruit species to be treated. It was found that, as is known in the art, the type of surfactant used is not critical. Any of the known types of surfactants may be used in the composition in accordance with the present invention as
- 25 long as they achieve an even distribution of the rest-breaking agents over the deciduous fruit species to be treated. By routine experimentation one of ordinary skill in the art can establish which surfactants work and which do not. As is known to the person skilled in the art, surfactants are typically classified as amphoteric, anionic, cationic, nonionic, and miscellaneous surfactants.
- 30 The reader is referred to the above-mentioned international patent publications

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and G.L. Hollis, ed., *Surfactants Europe, A Directory of Surface Active Agents available in Europe*, The Royal Society of Chemistry, Cambridge, 1995.

5 The alkoxyated amine surfactants and alkoxyated quaternary ammonium surfactants which are described in WO 94/23574 (i.e. on page 4, line 12, through page 8, line 17, and on page 12, lines 1-11), WO 96/01049 (i.e. on page 4, line 13, through page 8, line 10, and on page 12, lines 12-24), and WO 97/24926 (i.e. on page 4, line 24, through page 10, line 2) are particularly preferred for use in the invention composition. More preferably, an alkoxyated
10 amine is used in the composition in accordance with the present invention. Most preferably, Armoblen®, Armobreak®, and Beroi® compounds, which are commercially available from Akzo Nobel Chemicals, are used in the invention composition.

15 Preferably, the composition in accordance with the present invention comprises an organic nitrogen-containing compound selected from choline salts, an inorganic nitrate selected from potassium nitrate, calcium nitrate, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, zinc ammonium nitrate, and mixtures thereof, and a surfactant selected from alkoxyated
20 amines.

The composition of the present invention is typically applied to the deciduous fruit species prior to blossom. The optimum time to break rest for a particular deciduous fruit species will depend upon several factors including the type of
25 fruit, the cultivar, the climatic conditions, and the types and amounts of the rest-breaking agents being applied. For some fruit or cultivar species, the best rest-breaking effects are accomplished by early application of the rest-breaking composition, whereas for others it is best to wait until just before blossom. In general, the rest-breaking composition will be applied at some point between
30 the time when winter has peaked and the time when blossoming begins.